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Abstract:

Coal-based activated carbons (CAC) were prepared from coal in Xinjiang China by microwave-assisted activation. The effects of preparation conditions on adsorption capabilities of CAC for methylene blue (MB) and iodine were investigated. The microwave activation was carried out with coal alkali ratio (CAR) of 1:3 for 12 min at 700 W of power, the adsorption capacities of the prepared CAC achieved the maximal values of 312 and 1048.19 mg/g for MB and iodine. The increasing of CAR, activation time, and microwave power reduced the surface functional groups and improved the pH_{PZC} of CAC. The BET surface area and total pore volume of CAC prepared were identified as 1770.49 m^2/g and 0.99 cm^3/g, respectively. Hence, the work demonstrates that the use of microwave heating for preparing CAC is more rapid, cheaper and efficient. The adsorption behaviors of typical polycyclic aromatic hydrocarbons (PAHs) in ethanol aqueous solution on CAC were also explored. Equilibrium data were favorably described by the Langmuir and Freundlich isotherms, and adsorption kinetics was fitted to the pseudo-second-order model well. The equilibrium adsorption amounts were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and 78.18 mg/g for naphthalene. Thus, CAC prepared by microwave activation could have a very effective application in removal of these PAHs.

Key words: Coal-based activated carbon; Microwave activation; PAHs; Adsorption

1. Introduction

Activated carbons (AC) are porous material with extremely high surface areas; they have been widely used in a variety of industrial applications such as separation/purification of liquids and gases, removal of toxic substances, catalysts and catalyst support, super capacitors, electrodes and gas storage [1]. AC is usually prepared from different sources of raw materials utilizing different processing methods. Major raw materials for the preparation of AC are coal, petroleum, peat, wood and agricultural wastes. Among which, coal is the most commonly used precursor for AC production due to the advantage of its low cost of production and abundant resources as well as specific beneficial properties [2]. Furthermore, coal-based activated carbon (CAC) is greater demand since it has greater density, corrosion endurance, hardness and more durable than other AC [3]. Coal is an abundant resource with geological reserves exceeding 2.19 million tons. China accounts for 40% of the total reserves. Xinjiang Province in Northwest China has become a large-scale coal production base. The high quality of coals is characterized as low ash yields, low S contents, and low mineral contents [4]. Providing abundant and high quality raw materials is thus important for the development of high value-added coal chemical products. For this reason, coal is selected as a stable alternative for the preparation of AC in Xinjiang.

Generally, two methods are used for the preparation of ACs via physical and chemical activation. During physical activation, the raw material is carbonized first at high temperature and then it is activated by CO_2 or steam under pressure to increase porosity and surface area of ACs. In chemical activation both carbonization and activation takes place simultaneously, in which raw material is first impregnated with activating chemical and then carbonized at desired temperature that varies according to activating chemical used [5]. Conventional heating method is usually transferred from

surface into the interior of the material by thermal conduction using the tubular furnace at relatively high temperature and long time; as a result, the process of heating was slow, high energy consumption and non-uniform with the surfaces [6]. In recent years, microwave irradiation has been widely investigated due to the tremendous thermal gradient from the interior of the char particle to its cool surface allows the microwave-induced reaction to proceed more quickly and effectively at a lower bulk temperature [7]. Moreover, microwave radiation supply energy directly to carbon skeleton at molecular level. Thus, microwave heating provides additional advantages such as energy savings and shortening the processing time, possibility of selective heating, precise control of temperature, small equipment size and reduced waste comparing with traditional heating techniques [8, 9, 10, 11, 12, 13].

In microwave irradiation chemical activation, the raw material is first impregnated by activating agents such as H_3PO_4, KOH or $ZnCl_2$, followed by thermal activation to create the pore structure. The microwave induced chemical activation usually has higher carbon yield and better developed pore structure than the physical activation [14, 15, 16, 17]. Liu *et al.* [9] develop a microwave induced activation process for the preparation of high surface area bamboo-based AC. The optimal activation conditions were determined as: microwave power 350 W, radiation time 20 min and phosphoric acid/carbon ratio 1:1, under which a surface area of 1432 m^2/g could be reached. Li *et al.* [7] prepared relatively well developed porosity AC from tobacco stems by chemical activation with K_2CO_3 using microwave radiation. The optimum conditions were as follow: microwave power 700 W, microwave radiation time 30 min, K_2CO_3/C ratio 1.5:1. Wang *et al.* [10] has been successfully used to prepare AC from wood via microwave-induced $ZnCl_2$ activation. However, relatively few studies have focused on the preparation of CAC from anthracite by microwave activation. Revealing

the correlation between the microwave process conditions of preparing CAC and its adsorption performance is also necessary.

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds that have more than two aromatic rings in their molecules. PAHs can transport long distance in air and water, and some PAHs are capable of interacting with DNA to promote mutagenic and carcinogenic responses [18, 19]. Because of their stability and difficult degradation by microorganisms, it is difficult to remove PAHs using only biological treatment processes. Additionally, PAHs are not efficiently removed by conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration, or ozonation. AC is the most commonly used porous media for the removal of PAHs from solution [20-22]. Yuan *et al.* [23] reported that porous carbons were prepared from petroleum coke by KOH chemical activation and used as adsorbents for effective adsorbing naphthalene, fluorene, phenanthrene, pyrene and fluoranthene from aqueous solutions, at an initial concentration of 3250–6250 ng/mL, over 90% of PAHs are removed from the solution within 30 min. Kong *et al.* [20] reported that the performance of sesame stalk-based AC by potassium hydroxide in the efficient removal of phenanthrene from an aqueous solution, at a carbon concentration of 10 mg/32mL and a carbonization temperature of 700 °C, the removal efficiency of phenanthrene approached 100%, which was comparable to that by the commercial carbon. Cabal *et al.* [21] studied the preparation of AC from bean pods waste by chemical activation was investigated as adsorbents for the adsorption of naphthalene from water solutions at low concentration. Moreover, a number of studies have shown that AC prepared from different materials has significant differences in the adsorption of PAHs. The adsorption behavior of different PAHs on AC has some differences [24, 25, 26]. These three typical PAHs (naphthalene, phenanthrene, pyrene) were selected owing to their common

111 presence in the environment and their troublesome properties. These are taken as representatives of
112 two-, three- and four-ringed PAHs. It can be seen that these substances have low solubility in water,
113 which tends to be even lower when the number of aromatic rings is increased. Therefore, exploring
114 CAC prepared using microwave activation for the adsorption features of typical PAHs in 30%
115 ethanol aqueous solution is considerably interesting and informative.

116 The main purpose of the present study is to use rich anthracite from Xinjiang as raw material to
117 develop a microwave-induced activation process for the preparation of CAC with high surface area
118 and high adsorption performance to PAHs. The effects of activator types, coal alkali ratio (CAR),
119 activation time, and microwave power on the adsorption capabilities of CAC for MB and iodine
120 were investigated. CAC was characterized by using the Boehm method, point of zero charge,
121 nitrogen adsorption isotherm, and scanning electron microscopy (SEM). The adsorption features,
122 isotherm, and kinetics of typical PAHs such as naphthalene, phenanthrene, and pyrene were also
123 explored. The results were used to evaluate the potential application of CAC prepared by
124 microwave-induced activation for the removal of PAHs.

125 ## 2. Materials and methods

126 ### 2.1. Materials

127 This raw anthracite coal was purchased from TBEA, Changji, Xinjiang Uygur Autonomous
128 Region, China. The coal was passed through a 100 mesh sieve, washed with distilled water to
129 remove carbon and fines, and dried in an air oven at 110 °C for 4 h. The resultant coal powder was
130 used to prepare the CAC. The selected physio-chemical properties of naphthalene, phenanthrene and
131 pyrene are shown in Table 1. Naphthalene, phenanthrene and pyrene (>98%; Aladdin, Shanghai,
132 China) were used to prepare the stock solutions by dissolving an appropriate amount in 30% ethanol

aqueous solution.

Table 1 should be positioned here.

2.2. Preparation of CAC

CAC was prepared within a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. The oven was equipped with a power controller (100, 300, 500, 700, and 900 W) and a time controller (4, 8, 12, 16, and 20 min). The mixture of 10 g with various ratios (1:1, 1:2, 1:3, 1:4, and 1:5) of the dried coal powder to activator (KOH, $ZnCl_2$ and H_3PO_4) was placed in a quartzose tube of a microwave reactor to activate under vacuum atmosphere at the given power and time. The resultant products were washed with 10% hydrochloric acid and then with distilled water until the filtrate reached neutral. The remaining solid was dried in an oven at 110 °C for 4 h and stored in sealed glass bottles for the adsorption experiments.

The amount of MB adsorption is often regarded as a measure of its performance for high molar-mass species and was determined according to GB/T12496.10-1999 (Detection standard of activated carbon in China) [20]. On the other hand, the adsorption performance of activated carbons for low-molar mass species is generally indicated by the iodine number, which was determined at 303 K based on the Standard Detection Method (ASTM Designation: D4607-86) [20].

2.3. Characterization methods

The textural properties of the CAC were evaluated by measuring nitrogen adsorption isotherm at 77 K with ASAP 2020C surface area and porosity analyzer (Micromeritics Instrument Corp., USA). The S_{BET} was calculated using the BET equation. The total pore volume (V_t) was calculated by converting the adsorption amount at $P/P_0 = 0.95$ to a volume of liquid adsorbate. The micropore area (A_m) and volume (V_m) were obtained using the t-plot method. The external volume (V_e) was the

deduction of V_m from V_t and the external area (A_a) was the deduction of A_m from $S_{BET.}$ The surface morphology of the CAC was examined using scanning electron microscopy (SEM) (JSM-6490LV, Japan Electron Optics Laboratory Ltd. Corp., Japan) at accelerating voltages of 15 kV. Before observation, the samples were coated with gold in E-1010 Ion sputter. X-ray diffraction (XRD) was carried out on a Rigaku D/MAX-YA diffractometer with Ni-filtered Cu Ka radiation as the X-ray source.

The ‘‘Boehm titration’’ is a commonly used technique to determine the acidic oxygen surface functional groups on carbon samples whereby bases of various strengths ($NaHCO_3$, Na_2CO_3, NaOH) neutralize different acidic oxygen surface functionalities [19]. The weakest base, $NaHCO_3$, neutralizes only the strongest acidic carbon surface functionalities (CSFs) which are carboxylic groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups. The strongest base typically used, NaOH, neutralizes carboxylic, lactonic and phenolic groups. The number of each type of CSF can be determined by difference between the uptake of each reaction base [19]. A mixture of 1.5 g CAC and 25.00 mL of one of the three 0.05 M reaction bases, $NaHCO_3$, Na_2CO_3 and NaOH was filtered and wash with distilled water adequately after stirring for 24 h, then all the filtrate collected was added 0.05 M HCl to completely neutralize and end with methyl red indicator.

The point of zero charge (pH_{PZC}) is defined as the pH of the mixtures at which surface charge density on the adsorbent is zero. The pH_{PZC} values were determined by a mass titration method proposed by Franz [14]. Activated carbon (0.1 g) was added to 20 mL NaCl solutions, and then the initial pH had been adjusted with NaOH or HCl. The flasks were sealed and placed on a shaker for 24 h. The pH_{PZC} occurred when there was no change in the pH after contact with the carbon.

2.4. Adsorption experiments of PAHs

2.4.1. Adsorption performance analysis

Naphthalene, phenanthrene and pyrene were initially solved into ethanol aqueous solution (30 vol%) to prepare the 300 mg/L stock solutions, respectively. The concentrations of various adsorbate solutions were measured after adsorption by a UV–vis spectrophotometer (UV–752N, Shanghai Metash Instruments Co., Ltd, China). The concentration of naphthalene, phenanthrene and pyrene were calculated based on the following calibration equations, respectively: (1) at 218 nm, (2) at 249 nm, (3) at 237 nm. C = 1.7319A218 - 0.2309 (1), and R^2 was equal to 0.9995. C = 3.4483A_{249} + 0.0103 (2), and R^2 was equal to 0.9998. C = 3.4483A_{237} - 0.0469 (3), and R^2 was equal to 0.9998.

For each adsorption kinetics experiment, 40 mL of 300 mg/L adsorbate solution was placed in a 100 mL conical flask with a cover. The solution was shaken at 25 °C and 60 rpm. After preheating for 5 min, 100 mg of CAC prepared was added to the solution. Then, the samples were taken periodically and filtrated immediately by suction. The supernatant solution was analyzed for the remaining concentration of adsorbate by a UV–vis spectrophotometer.

For each adsorption isotherm experiment, approximately 40 mL of different adsorbate solution of various concentrations was placed in a 100 mL conical flask with cover. To establish the thermal equilibrium before adsorption, the solution was shaken at 25 °C and a stirring rate of 60 rpm. After preheating for 5 min, 150 mg of CAC prepared was added to the solution. Then, the samples were taken after 50 min and filtrated immediately by suction. The supernatant solution was analyzed for the remaining concentration of adsorbate by a UV–vis spectrophotometer. The amount of adsorbate (Q_e) was calculated as follow:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 (mg/L) and C_e (mg/L) are liquid-phase concentrations of adsorbate at initial and

199 equilibrium, respectively. V (mL) represents the volume of the solution and m (g) stands for the mass
200 of CAC used.

201 2.4.2. Adsorption isotherm

202 The Langmuir adsorption Eq. (2), predicts the existence of monolayer coverage of the adsorbate
203 at the outer surface of the adsorbent [9].

204 $$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

205 where C_e and Q_e are as defined in Eq. (1), q_m is adsorption maximum (mg/g); K_L is sorption
206 equilibrium constant (L/mg).

207 The Freundlich isotherm [9] is an empirical equation employed to describe heterogeneous
208 systems, and is expressed by the following Eq. (3):

209 $$\log Q_e = \frac{1}{n} \log C_e + \log K_F \qquad (3)$$

210 where K_F is a constant which represents a measure of the adsorption capacity of the adsorbent for
211 specific solute, and n is a measure of intensity of adsorption.

212 2.4.3. Adsorption kinetics

213 Kinetic models are used to examine the rate of the adsorption process and potential rate
214 controlling step, i.e., particle diffusion or chemical reaction. The capability of pseudo-first-order,
215 pseudo-second-order and intraparticle diffusion, were examined in this study.

216 The pseudo-first-order kinetic rate equation is expressed as [15]:

217 $$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{k_1}{Q_e t} \qquad (4)$$

218 where k_1 is the rate constant of pseudo-first-order sorption (min), which can be determined from the
219 slope of the linearized pseudo-first-order rate equation.

The pseudo-second-order kinetic rate equation is expressed as [15]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\ 2}} + \frac{t}{Q_e} \qquad (5)$$

where k_2 is the second-order rate constant (g/mg/min) can be determined from the intercept of the linearized pseudo-second-order rate equation.

In the intraparticle diffusion model, the relationship between the adsorption capacity at time t, Q_t and $t^{1/2}$ could be written as [27]:

$$Q_t = K_p\, t^{1/2} + C \qquad (6)$$

where K_p is the intraparticle diffusion constant (mg/g/min$^{1/2}$) and C is the intercept of the line, which is proportional to the boundary layer thickness.

3. Results and discussion

3.1 Preparation of CAC

3.1.1. Effects of activator

MB molecule has been estimated that the minimum pore size it can enter is 1.3 nm [28] and can be used to indicate the capacity of a carbon for sorption of medium-sized molecules. The iodine molecule provides information about the surface area that is contributed by pores larger than 1 nm [29], and the iodine number provides a good indication of the capacity of a carbon for sorption of small molecules [30]. The average pore width of KOH-activated CAC was approximately 2.8 nm in Table 2, which was a sufficiently large pore width to allow MB and iodine molecules to pass through for a large amount of adsorption.

According to the preliminary experiment, the ratio for $ZnCl_2$ or H_3PO_4 was also 1:3, whose is optimum conditions are the same as KOH. The influences of activator types on the adsorption amounts of MB and iodine on CAC prepared at a coal activator ratio of 1:3, activation time of 12

min, and microwave power of 700 W are shown in Fig. 1. In the chemical activation, the adsorption property of CAC prepared with various activating agents showed a significant difference. The adsorption amounts of MB and iodine on CAC prepared with KOH reached the maximum. Alkaline hydroxide activation involves the redox reduction and carbon oxidation to generate porosity. During the reactions, the evolution of CO, CO_2 and H_2 constituents, and additional reactions [11] between the active intermediates with the carbon surface are possible (Eqs. (1) - (3)).

$$6KOH + C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad (1)$$

$$K_2CO_3 + C \rightarrow K_2O + 2CO_2 \quad (2)$$

$$2K + CO_2 \rightarrow K_2O + 2CO \quad (3)$$

The produced alkaline is intercalated to the carbon matrix responsible for both stabilization and widening of the spaces between the carbon atomic layers. Thus, KOH activated samples exhibited the best adsorption capacity. Metallic potassium formed during the redox reaction can be intercalated into the carbon walls independently of the structural order responsible for separation and degradation of graphitic layers thus develop the microporosity and mesoporosity. The resulting CAC by the activation agents of $ZnCl_2$ and H_3PO_4 had very low adsorption amounts of MB and iodine (particularly the adsorption amounts of MB), which may be due to the activation of $ZnCl_2$ and H_3PO_4 producing a lower specific surface area and smaller pore size on CAC, which is showed in Table 2. The activation agents of $ZnCl_2$ and H_3PO_4 could be widely used to prepare AC from lignocellulosic products [31]. So KOH was selected as appropriate activator in this investigation.

Table 2 should be positioned here.

Fig. 1 should be positioned here.

3.1.2. Effects of coal to KOH ratio (CAR)

Table 3 presents the influences of the CAR on the adsorption amounts of MB and iodine on CAC prepared at microwave power of 700 W for 8 min. The activation reaction was strengthened and a large number of pores were formed with the rising ratio, enhancing the CAC adsorption capacity. When CAR reached 1:3, the carbons on the active sites could be reacted completely, and the adsorption capacity reached the maximum [7]. When CAR was larger than 1:3, the pores were widened. Besides, excessive KOH molecules might decompose following the reactions:

$$2KOH \rightarrow K_2O + H_2O \quad (4)$$

$$H_2O + C \rightarrow CO + H_2 \quad (5)$$

Therefore, the catalytic oxidation entailed the widening of mesoporous structures and carbon burn off, so the adsorption capacity of AC was decreased.

Surface functional groups such as phenolic group (-OH), lactonic group (-COOCO-), and carboxylic group (-COOH) were determined by Boehm titration. The results of these surface functional groups for CAC with various CARs are shown in Table 3. The CAR apparently had a destructive influence on the functional groups of CAC. With increased CAR, the amount of lactonic groups, phenolic and carboxylic groups decreased, and phenolic and carboxylic groups are fairly low. A possible explanation for this could be that the alkali activator affected the number of surface acidic functional groups. The results of pH_{PZC} titrations for CAC under various CARs can also be seen in Table 3. pH_{PZC} increased with increased CAR. Previous research has indicated that the existence of surface functional groups, such as carboxyl, carbonyl, and phenol, constitutes the source of surface acidity [9, 12, 32] and the opposite is observed for alkali treatment. Considering the results of the adsorption capacity of CAC, CAR was set at 1:3 for this study.

3.1.3. Effects of activation time

Table 3 demonstrates the effects of activation time on the adsorption amounts of MB and iodine on CAC prepared with CAR of 1:3 at microwave power of 700 W. The MB adsorption amounts of CAC increased from approximately 234 to 312 mg/g with increased activation time from 4 to 12 min, and then decreased to 238.5 mg/g for 20 min activation. Similarly, the iodine number of the CAC increased gradually from approximately 962.12 to 1048.19 mg/g with increased time from 4 to 12 min, and then slightly decreased to 1045.87 mg/g for 20 min activation. However, when the activation time reached a certain value, the carbon pores were burnt off by microwave heating, thereby lowering the CAC adsorption capacity. A similar tendency was observed in the preparation of AC from rice husk [17].

The results of the surface functional content and pH_{PZC} titrations for CAC under various activation times can be seen in Table 3. With increased activation time from 4 to 20 min, the number of surface functional groups decreased. pH_{PZC} generally showed the opposite trend. The phenomenon implied that increasing activation time promoted an acceleration of energy, leading to a destruct of surface functional groups and developed the rudimentary of the pore structure [11]. Considering the results of the CAC adsorption capacity, the activation time was set at 12 min in this study.

3.1.4. Effects of microwave power

The effects of microwave power on the adsorption amounts of MB and iodine of CAC prepared by KOH activator with CAR of 1:3 for 12 min, as shown in Table 3. The adsorption amounts of MB rose from 54 to 312 mg/g with increased power from 100 to 700 W and then decreased. The adsorption amounts of iodine increased from 769.02 to 1048.19 mg/g with increased power from 100 to 700 W and then decreased. More carbon molecules were activated along with the higher

microwave power participate in the activation reaction, and lead to the development of pore structure adequately. However, the exceeded of a certain power may lead to excessive destruction of pore structure [11].

The results of the surface functional content and pH_{PZC} titrations for CAC under various microwave powers can be seen in Table 3. With increased microwave power from 100 to 900 W, the number of lactonic groups decreased. The surface functional content and pH_{PZC} had the opposite trend. Menéndez *et al.* [12] pointed out that microwave treatment reduced the functional group, especially those of acidic in nature, and increased the pH_{PZC} of the carbon. In this study, CAC produced directly by microwave heating agreed with the reported findings [12]. The optimum microwave power in this experiment was thus 700 W.

Table 3 should be positioned here.

3.2. Characterization of CAC

3.2.1. Porous structure analysis

The N_2 adsorption isotherms of the CAC at 77 K are presented in Fig. 2. The adsorption isotherms demonstrated a sharp rise at low P/P_0 range, and a gradual increase was seen at relatively high P/P_0 range. According to the classification of IUPAC [33], all adsorption isotherms were of type I, indicating that the CACs were mainly microporous. The N_2 adsorption isotherms on activated carbons from Zonguldak region coals using chemical activation also conformed to type I isotherm by Kopac and Toprak [3]. Moreover, the saturated adsorption amounts of N_2 increased after microwave activation, implying an increase in the pore volume.

The textural properties obtained from the N_2 adsorption isotherms are summarized in Table 2. CAC-4 had a well-developed porosity with a surface area of 1770.49 m^2/g, which was primarily

microporous under optimal conditions. Liu *et al.* [9] reported that bamboo-based AC using microwave radiation has a maximum surface area of 1409 m^2/g. Yagmur *et al.* [13] reported that the maximum BET surface area was 1157 m^2/g for the AC from waste tea treated with chemical activation with microwave energy. Compared with previous works, CAC obtained a higher specific surface area. This observation suggested that coal could also form a considerable porous structure through microwave-assisted chemical activation. The specific surface area obtained by the BET equation (S_{BET}), micropore area (A_m), external surface area (A_e), micropore volume (V_m), and total pore volume (V_t) of CAC-2 were larger than those of CAC-1, whereas the average pore width of CAC-2 was smaller than CAC-1. This result indicated that the increasing potassium hydroxide amount enhanced the pore development and created new pores of coal, resulting in further increased specific surface area and decreased average pore width. CAC-2, CAC-3, and CAC-4 were obtained using different activation times. With increased activation time from 4 min to 12 min, the S_{BET}, A_e, and V_t gradually increased. The A_m and V_m of CAC-2 and CAC-4 had no significant differences, and they were larger than those of CAC-3 but not significantly. The phenomenon implied that the increase in activation time promotes an acceleration of energy, which in turn increases the reaction rates, thus developed the rudimentary of the pore structure [11]. The six surface physical parameter values of CAC-5 prepared at 100 W of microwave power were small, indicating no strong reaction occurred between the coal and activation agent at low microwave power.

Fig. 2 should be positioned here.

Enhancing microwave power from 100 to 700 W drastically improved textural properties, possibly ascribed to the combined effect of internal and volumetric heating responsible for the expansion of carbon structure [11]. Also, considerable changes in the surface properties were

achieved within a short time, which should be attributed to the distinct mechanism of microwave heating. As listed in **Table 4**, the samples obtained by microwave heating have higher BET surface area. It can be seen advantage of microwave heating is that the treatment time as well as the consumption of gases used in the treatment can be considerably reduced, which resulted in a reduction in the energy consumption, compared with conventional surface heating. In addition, microwave heating technique has overall shown better effect in terms of porous structure, relatively greater surface area than conventional heating method [3]. Hence, the work reported here clearly demonstrates that the use of microwave heating for preparation CAC is more rapid, cheaper and efficient than the use of a conventional furnace.

Table 4 should be positioned here.

3.2.2. Surface morphology analysis

SEM images of the coal and CAC prepared under optimum conditions (CAC-4) are shown in Fig. 3. The surface of raw material (Fig. 3(A)) was fairly smooth without any pores except for some occasional cracks. After activation, it shows the obtained CAC has an irregular surface with pores and craters. From Table 2, it was also known that the pores are micro- and mesopores. As shown in Fig. 3(B), the external surface of the CAC-4 demonstrated a well pronounced pore structure, indicating constitution of new matrix during the activation stage.

Fig. 3 should be positioned here.

3.2.3. Crystal structure

X-ray diffraction technique is a powerful tool to analyze crystalline nature of materials. Fig. 4 shows the XRD profiles of coal and CAC-4. The coal shows an intense diffraction peaks at 26°. The CAC-4 prepared from coal via microwave-induced KOH activation shows an intense diffraction

peaks at around 29° and several not obvious diffraction peaks at around 44°, corresponding to the (002) and (100) diffraction of disordered stacking of micrographites, respectively [14].

Fig. 4 should be positioned here.

3.3. Adsorption isotherm of selected PAHs on CAC-4

Table 5 lists the parameters of the Langmuir and Freundlich adsorption isotherm models of naphthalene, phenanthrene, and pyrene in ethanol aqueous solution onto CAC-4 at 25 °C, along with their regression coefficients (R^2), the adsorption capacity and sorption equilibrium constants (q_m and K_L), and intensity parameters (K_F and n). R^2 reflected the goodness of fit of each of the models to the data. For the Langmuir isotherm, the R^2 values were >0.9934. The regression coefficients R^2 of the Freundlich isotherm were >0.9809. Both Langmuir and Freundlich isotherm models efficiently predicted the adsorption of the three PAHs on CAC-4 with high correlation coefficients. This observation indicated that the sorption of naphthalene, phenanthrene, and pyrene onto CAC-4 may be confined to a monolayer adsorption and heterogeneous sorption. Similarly, adsorption isotherm of PAHs from vegetable oil on AC also fitted well by both isotherm models [26]. While Yuan *et al.* [22] reported that the equilibrium adsorption isotherms of PAHs from water on petroleum coke-derived porous carbon fitted the Freundlich equation well, and Kong *et al.* [20] reported that the phenanthrene removal from aqueous solution on sesame stalk-based carbon fit the Freundlich equation well.

With carbon, the sorption process results from molecular interactions between the carbon surface and the adsorbate, such as van der Waals attractions, electrostatic forces, and weak intermolecular association [34]. The properties of the adsorbate greatly influence the sorption process. Since PAHs are nonpolar compounds, sorption is governed mainly by hydrophobic interactions [24]. The values

of K_L, K_F, and q_m followed the trend of pyrene > phenanthrene > naphthalene, which confirmed that hydrophobic interactions follow the same trend. Kong *et al.* [20] reported that the hydrophobic interactions were the key factor for phenanthrene removal from aqueous solution by the sesame stalk-based carbon. Moreover, the values of n were all greater than 1 and did not significantly change, showing that the prepared CAC favorably adsorbed the three PAHs [22].

Table 5 should be positioned here.

3.4. Adsorption kinetics of selected PAHs on CAC-4

Fig. 5 shows the plots of the adsorption amounts of naphthalene, phenanthrene, and pyrene at different time intervals. The adsorption process consisted of two distinguished periods. In the first stage, the three PAHs were rapidly adsorbed onto easily accessible hydrophobic sites in the CAC-4 matrix within 5 min. In a well-stirred, solid–liquid system, the first stage of diffusive transport of PAHs molecules from the bulk solution to the exterior surface of porous CAC particles, as well as the intraparticle diffusion of the PAHs through the interior pores of CAC, were assumed to be rapid. In the second stage, adsorption was probably limited by the slow migration of adsorbates to less accessible sites associated with micropores within the CAC-4 matrix, which could take a long time. Valderrama *et al.* [25] reported similarly that the adsorption process of PAHs onto granular AC also was the two-stage. The adsorption amount increased with increased contact time. The maximum adsorption was observed at 20 min, beyond which almost no further increase in the adsorption amount was observed.

The experimental data for the naphthalene, phenanthrene, and pyrene adsorption onto CAC-4 were fitted by three kinetic models, the values of k_1, k_2, k_p, and Q_e, and the correlation coefficients are listed in Table 6. The experimental kinetic data followed the pseudo-second-order kinetic curves

418 for the three PAHs, which can be demonstrated by higher R^2 (>0.9999) and closer Q_e values to the
419 experimental ones, q_{exp}. The adsorption progress of the PAHs on the CAC surface were presumably
420 caused by the chemical interaction [14]. Cabal *et al.* [21] found the experimental data of adsorption
421 kinetics of aqueous naphthalene on the AC were fitted to the pseudo-second kinetic model with a
422 high correlation coefficient. While a literature showed that sorption systems of naphthalene and
423 pyrene on AC followed a pseudo-first-order reaction model, although the pseudo-second-order
424 reaction model provides an acceptable description of the sorption process [25]. The equilibrium
425 adsorption amounts at 20 min were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and
426 78.18 mg/g for naphthalene, respectively, decreased as follows: pyrene > phenanthrene >
427 naphthalene. Compared with the carbonaceous materials such as the phenanthrene adsorption
428 amount at 24 h from aqueous solution of sesame stalk- based AC was 73.74 mg/g [20], the
429 naphthalene adsorption amount at 60 min from aqueous solution of reed straw- based AC was 107.00
430 mg/g [35], and the pyrene adsorption amount at 24 h from aqueous solution of rice husk- based AC
431 was 104.50 mg/g [36], the PAHs adsorption performance of prepared carbon in this work was higher
432 and faster. In addition, coal as a precursor is relatively cheaper. Thus, these results indicate that CAC
433 prepared with microwave activation had excellent capability to remove PAHs from aqueous solution.
434 The agreement between the equilibrium adsorption values determined (q_{exp}) and the adsorption
435 maximum (q_m) obtained from the Langmuir isotherm was clear and sufficient. The observed trend in
436 adsorption amounts was generally consistent with the trend in the amount of aromatic rings and
437 molecular weight shown in Table 2. The adsorption amounts were higher for larger molecular PAHs
438 such as pyrene, which suggested that the PAHs were able to form a π-π complex between the
439 π-electrons of benzene rings and active sites on the AC surface [18]. Therefore, the π-π dispersive

interactions between the aromatic ring in PAHs and the graphene layers on CAC were the key parameters that determined the adsorptive affinity of those molecules with a polycyclic aromatic skeleton structure [19]. This phenomenon can explain why molecules with more aromatic rings showed a significantly higher adsorptive affinity than aromatics with fewer rings. The electron donor–acceptor mechanism could involve lactonic groups that predominated on the basic carbon surface. Lactonic groups acted as electron donors. The aromatic rings in the adsorbate accepted electrons [21], consistent with the number of lactonic groups and pH_{PZC} CAC-4 prepared at 0.35 mmol/g and 8.35, respectively.

Fig. 5 should be positioned here.

Table 6 should be positioned here.

4. Conclusions

1. The optimum conditions for CAC preparation were identified to be KOH activator, CAR of 1:3, activation time of 12 min, and microwave power of 700 W. Under the optimum conditions adsorption amounts of MB and iodine on CAC was 312 and 1048.19 mg/g, respectively.
2. The CAR, activation time, and microwave power destructed surface functional groups and raised the pH_{PZC} of CAC. The BET surface area and pore volume of the optimal CAC were evaluated as 1770.49 m^2/g and 0.99 cm^3/g, which was primarily microporous. The SEM image of the optimal CAC showed that the external surface of CAC had a well-pronounced and almost uniform pore structure. Hence, the work clearly demonstrates that the use of microwave heating for preparing CAC is more rapid, cheaper and efficient.
3. The adsorption equilibrium of naphthalene, phenanthrene, and pyrene on CAC-4 was satisfactorily represented by both the Langmuir and Freundlich isotherm models with high

correlation coefficients. The prepared CAC favorably adsorbed naphthalene, phenanthrene, and pyrene. The experimental kinetic data followed the pseudo-second-order kinetic curves for naphthalene, phenanthrene, and pyrene, presuming that the adsorption progress is affected by chemical interactions. The equilibrium adsorption amounts were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and 78.18 mg/g for naphthalene. Overall, CAC from Xinjiang region coal prepared by microwave activation could be effectively applied in liquid-phase adsorption involving PAHs.

Acknowledgements

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Figure captions:

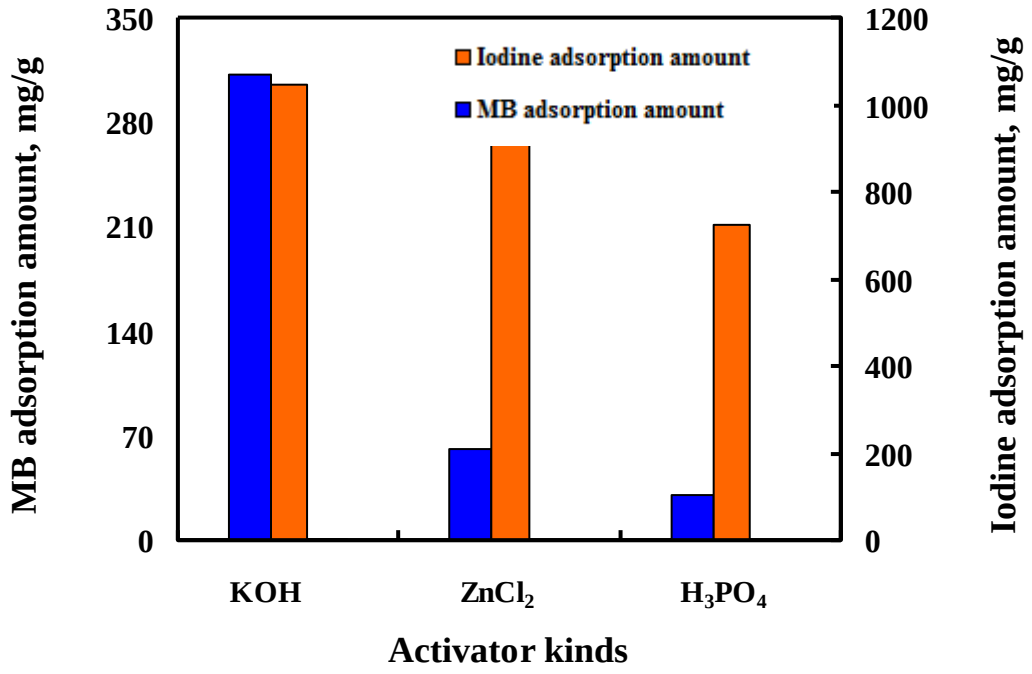
Fig. 1 Adsorption amounts of MB and iodine by CAC with various activator types (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

Fig. 2 Nitrogen adsorption isotherm for the prepared CACs (CAC-1: activation time = 8 min; microwave power = 700 W; CAR= 1:1, CAC-2: activation time = 8 min; microwave power = 700 W; CAR= 1:3, CAC-3: activation time = 4 min; microwave power = 700 W; CAR= 1:3, CAC-4: activation time = 12 min; microwave power = 700 W; CAR= 1:3, CAC-5: activation time = 12 min; microwave power = 100 W; CAR= 1:3).

Fig. 3 SEM micrographs of the selected samples at 5000× magnification: (A) coal, (B) CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

Fig. 4 XRD profiles of coal and CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

Fig. 5 Adsorption amounts of naphthalene, phenanthrene and pyrene in ethanol aqueous solution on CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3) at various times and at 25 °C.



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594 Fig. 1 Adsorption amounts of MB and iodine by CAC with various activator types (preparation

595 conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

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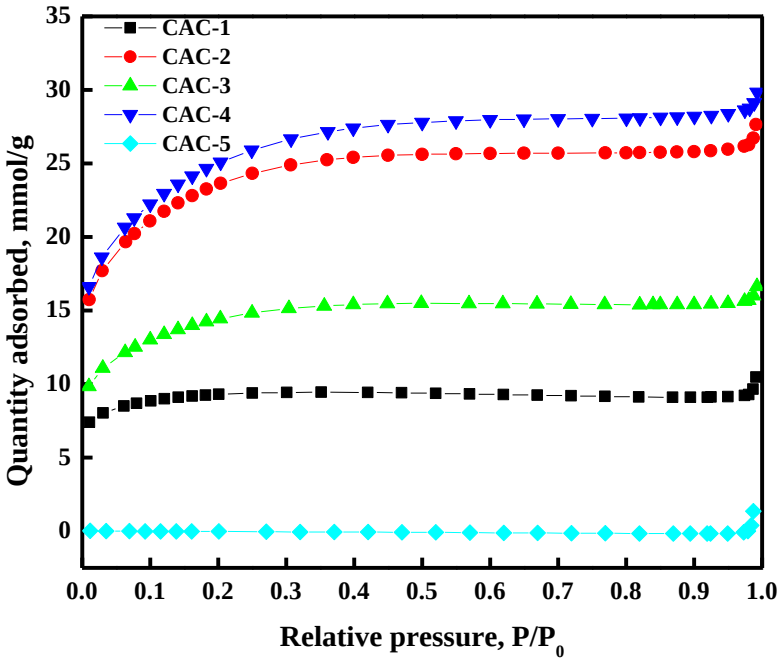


Fig. 2 Nitrogen adsorption isotherm for the prepared CACs (CAC-1: activation time = 8 min; microwave power = 700 W; CAR= 1:1, CAC-2: activation time = 8 min; microwave power = 700 W; CAR= 1:3, CAC-3: activation time = 4 min; microwave power = 700 W; CAR= 1:3, CAC-4: activation time = 12 min; microwave power = 700 W; CAR= 1:3, CAC-5: activation time = 12 min; microwave power = 100 W; CAR= 1:3).

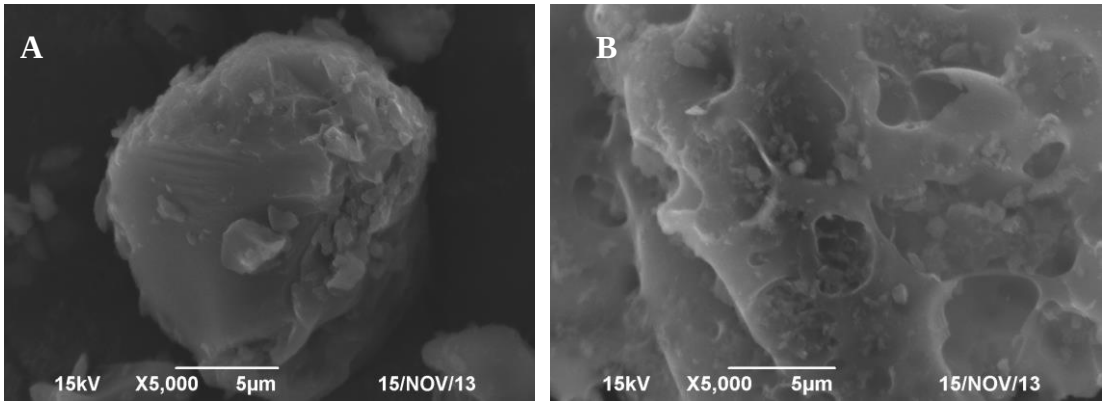
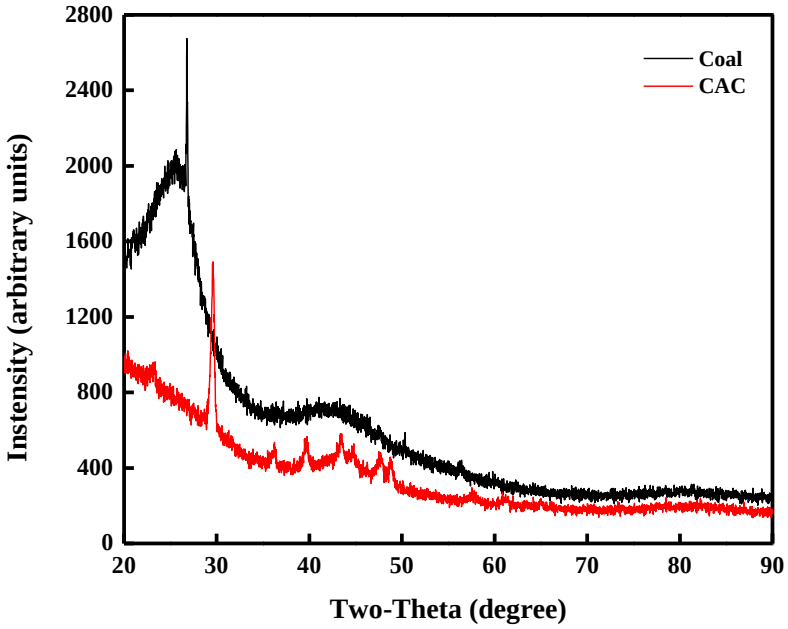


Fig. 3 SEM micrographs of the selected samples at 5000× magnification: (A) coal, (B) CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).



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616 Fig. 4 XRD profiles of coal and CAC-4 (preparation conditions: activation time = 12 min;

617 microwave power = 700 W; CAR= 1:3).

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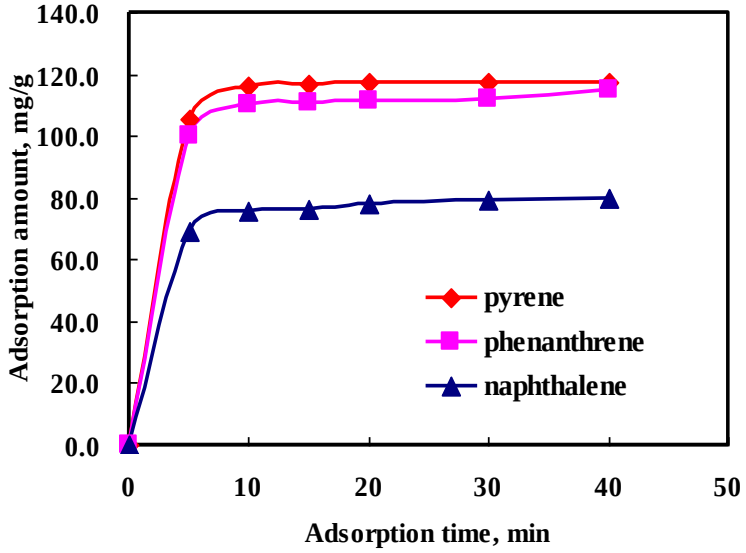

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621 Fig. 5 Adsorption amounts of naphthalene, phenanthrene and pyrene in ethanol aqueous solution on

622 CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3) at

623 various times and at 25 °C.

Table 1 Selected properties of PAHs used [22]

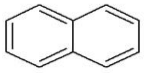
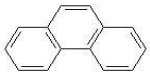
PAHs	Structure	Formula	Molecular weight (g/mol)	Molecular dimension (nm×nm×nm)	Malar volume (cm^3/mol)	Water solubility (ng/g)	logKow
Naphthalene		$C_{10}H_8$	128.17	0.91×0.73×0.38	148	30800	3.30
Phenanthrene		$C_{14}H_{10}$	178.22	1.17×0.80×0.34	199	1283	4.57
Pyrene		$C_{16}H_{10}$	202.25	0.92	214	135	5.18

Table 2 Activation conditions and surface characteristics of the prepared CACs.

Sample	Activation conditions			S_{BET}	A_m	A_e	V_m	V_t	V_m/V_t	Average pore width
	Microwave time min	Microwave power W	Coal activator ratio	m^2/g	M^2/g	M^2/g	cm^3/g	cm^3/g	%	nm
CAC-1	8	700	1:1	623.84	417.31	206.53	0.23	0.32	71.88	3.25
CAC-2	8	700	1:3	1651.50	543.09	1108.40	0.33	0.91	36.26	2.86
CAC-3	4	700	1:3	1007.27	379.35	627.92	0.22	0.54	40.74	2.86
CAC-4	12	700	1:3	1770.49	508.87	1261.62	0.61	0.99	61.62	2.82
CAC-5	12	100	1:3	0.21	0.00	0.00	0.00	0.00	0.00	0.00
CAC-6	12	700	1:3	934.54	425.64	534.22	0.37	0.49	75.51	1.95
CAC-7	12	700	1:3	843.56	384.34	423.55	0.31	0.42	73.81	1.88

S_{BET}: specific surface area obtained by BET equation, A_m, A_e: micropore area, external surface area, V_m, V_t: micropore volume, total pore volume.

Activator: The CAC-1, CAC-2, CAC-3, CAC-4, CAC-4 and CAC-5 with KOH; the CAC-6 with $ZnCl_2$; the CAC-7 with H_3PO_4.

644 Table 3 Adsorption performance and surface properties of CAC prepared with various CAR,
645 activation time and microwave power.

Treatments		MB adsorption amount (mg/g)	Iodine adsorption amount (mg/g)	Lactonic group (mmol/g)	Carboxylic groups (mmol/g)	Phenolic groups (mmol/g)	pH_{PZC}
CAR	1:1	77.7	999.38	0.5667	0.0333	0.0812	8.10
	1:2	268.5	1034.24	0.4933	0.0167	0.0530	8.20
	1:3	291.0	1038.90	0.4700	0.0063	0.0233	8.30
	1:4	270.0	1034.23	0.3500	0.0056	0.0100	8.35
	1:5	256.5	1017.95	0.2333	0.0028	0.0067	8.30
Activation time (min)	4	234.0	962.12	0.5267	0.0900	0.0267	8.10
	8	282.0	1033.54	0.4700	0.0733	0.0190	8.30
	12	312.0	1048.19	0.3500	0.0700	0.0058	8.35
	16	238.5	1045.87	0.2267	0.0333	0.0047	8.32
	20	241.5	1045.87	0.1833	0.0083	0.0033	8.31
Microwave power (W)	100	54.0	769.02	0.5733	0.0933	0.0562	7.50
	300	180.0	1003.99	0.4567	0.0267	0.0333	7.60
	500	210.0	1031.91	0.4133	0.0133	0.0193	7.90
	700	312.0	1048.19	0.3500	0.0093	0.0097	8.35
	900	219.0	1043.54	0.3333	0.0045	0.0033	8.30

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Table 4 Comparison of different kinds of ACs.

Sample	Carbon source	Heating methods	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Data sources
Commercial AC	Pitch	Convention	1403.00	0.583	[19]
Commercial AC	Wood	Convention	1100.00	1.061	[19]
Lotus stalk based - AC	Lotus stalk	Convention	1220.00	1.191	[14]
Jatropha hull based - AC	Jatropha hull	Convention	748.00	0.580	[2]
CAC	Coal	Convention	830.5m^2/g	0.250	[3]
Rice husk based - AC	Rice husk	Microwave	752.00	0.640	[37]
Cotton stalk based - AC	Cotton stalk	Microwave	729.33.00	0.380	[38]
CAC	Coal	Microwave	1770.49	0.990	This work

Table 5 Isotherm constants for the adsorption of naphthalene, phenanthrene, and pyrene in ethanol aqueous solution onto CAC-4 at 25 °C.

PAHs	Langmuir			Freundlich		
	K_L(L/mg)	q_m(mg/g)	R^2	K_F(L/mg)	n	R^2
Naphthalene	0.03	89.29	0.9934	5.50	1.71	0.9921
Phenanthrene	0.28	116.28	0.9990	24.62	1.60	0.9848
Pyrene	0.90	117.65	0.9991	52.16	1.61	0.9809

Table 6 Kinetics constants for the adsorption of naphthalene, phenanthrene, and pyrene in ethanol aqueous solution onto CAC-4.

PAHs	q_{exp} (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
		k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg min)	Q_e (mg/g)	R^2	k_p (mg/g/ $min^{1/2}$)	R^2
Naphthalene	78.18	0.61	80.65	0.9615	0.02	81.30	0.9999	1.84	0.9125
Phenanthrene	111.39	0.25	112.36	0.9970	0.04	112.36	1.0000	0.76	0.9124
Pyrene	117.17	0.13	117.65	0.9644	0.06	117.65	1.0000	0.61	0.9049